

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-026832  
 (43)Date of publication of application : 27.01.1998

(51)Int.CI. G03F 7/32  
 G03F 7/42  
 H01L 21/027  
 H01L 21/304  
 H01L 21/308

(21)Application number : 08-199574 (71)Applicant : TOKYO OHKA KOGYO CO LTD  
 (22)Date of filing : 11.07.1996 (72)Inventor : TANABE MASAHIKO  
 WAKIYA KAZUMASA  
 KOBAYASHI MASAICHI  
 NAKAYAMA TOSHIMASA

**(54) RINSING SOLUTION COMPOSITION FOR LITHOGRAPHY AND TREATMENT OF SUBSTRATE WITH THE SAME**

**(57)Abstract:**

**PROBLEM TO BE SOLVED:** To obtain a rinsing soln. compsn. not corroding the metallic thin film of a substrate by using a water-soluble org. solvent and water.

**SOLUTION:** This rinsing soln. compsn. used for rinsing a substrate for production of a semiconductor device or a liq. crystal panel device subjected to peeling treatment with a hydrofluoride-contg. peeling soln. contains 20-90wt.%, preferably 40-80wt.% water-soluble org. solvent and 10-80wt.%, preferably 20-60wt.% water. The org. solvent is preferably at least one selected from among alcohol, glycol monoether and an aprotic polar solvent. It is especially preferably monohydric alcohol such as methanol, ethanol or isopropanol.

**LEGAL STATUS**

[Date of request for examination]	05.10.2001
[Date of sending the examiner's decision of rejection]	06.06.2003
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3755776
[Date of registration]	06.01.2006
[Number of appeal against examiner's decision of rejection]	2003-12744
[Date of requesting appeal against examiner's decision of rejection]	04.07.2003
[Date of extinction of right]	

THIS PAGE BLANK (ASPC)

\* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

[JP,10-026832,A]

**CLAIMS**

[Claim(s)]

[Claim 1] The rinse constituent for lithography characterized by being a rinse constituent for carrying out rinse processing of the substrate which processed the salt of a hydrofluoric acid and the base which does not contain a metal with the exfoliation liquid used as a major component, and being the constituent with which said rinse constituent contains a water-soluble organic solvent and water.

[Claim 2] The rinse constituent for lithography according to claim 1 characterized by being at least one sort as which a water-soluble organic solvent is chosen from alcohols, glycol mono-ether, and an aprotic polar solvent.

[Claim 3] The rinse constituent for lithography according to claim 2 characterized by alcohols being methyl alcohol, ethyl alcohol, isopropyl alcohol, and ethylene glycol.

[Claim 4] The rinse constituent for lithography according to claim 2 characterized by glycol mono-ether being the diethylene-glycol monobutyl ether.

[Claim 5] The rinse constituent for lithography according to claim 2 characterized by aprotic polar solvents being dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, a N-methyl-2-pyrrolidone, and 1,3-dimethyl-2-imidazolidinone.

[Claim 6] The exfoliation liquid which uses as a major component the salt of a hydrofluoric acid according to claim 1 and the base which does not contain a metal (a) The salt of a hydrofluoric acid and the base which does not contain a metal, (b) dimethyl sulfoxide, N.N-dimethylformamide, N,N-dimethylacetamide, a N-methyl-2-pyrrolidone, At least one sort chosen from 1,3-dimethyl-2-imidazolidinone, ethylene glycol, and the diethylene-glycol monobutyl ether, The rinse constituent for lithography according to claim 1 characterized by being the exfoliation liquid for resists which contains (c) water in a list and has the hydrogen-ion density (pH) in the range of 5-8.

[Claim 7] The rinse constituent for lithography according to claim 1 characterized by the exfoliation liquid which uses as a major component the salt of a hydrofluoric acid according to claim 1 and the base which does not contain a metal being the exfoliation liquid for resists containing 0.2 - 10 % of the weight of ammonium fluorides, 30 - 90 % of the weight of dimethyl sulfoxide, and 5 - 50 % of the weight of water.

[Claim 8] The rinse constituent for lithography according to claim 1 to 7 characterized by a rinse constituent containing 20 - 90 % of the weight of water-soluble organic solvents, and 10 - 80 % of the weight of water.

[Claim 9] The rinse constituent for lithography characterized by a rinse constituent according to claim 1 containing anticorrosives further.

[Claim 10] The rinse constituent for lithography according to claim 9 characterized by being at least one sort as which anticorrosives are chosen from a catechol, 2-butine -1, 4-diol, benzotriazol, and D-sorbitol.

[Claim 11] The rinse constituent for lithography characterized by a rinse constituent according to claim 9 containing 55 - 85 % of the weight of water-soluble organic solvents, 10 - 40 % of the weight of water, and 0.5 - 15 % of the weight of anticorrosives.

[Claim 12] The art of the substrate characterized by processing at each following process after preparing a desired resist pattern on a substrate and carrying out etching processing.

(I) Process which carries out washing processing with the process (III) water which carries out rinse processing of the process (II) substrate which processes a salt with the base which does not contain a hydrofluoric acid and a metal for a resist pattern with the exfoliation liquid used as a major component with the rinse constituent for lithography containing a water-soluble organic solvent and water [claim 13] The art of the substrate characterized by being the exfoliation liquid for resists which contains at least one sort as which the exfoliation liquid of the (I) process in an art according to claim 12 is chosen from the salt, (b) dimethyl sulfoxide, the N,N-dimethylformamide, the N,N-dimethylacetamide, the N-methyl-2-pyrrolidone, the 1,3-dimethyl-2-imidazolidinone, the ethylene glycol, and the diethylene-glycol monobutyl ether of the (a) hydrofluoric acid and the base which does not contain a metal, and (c) water, and has the hydrogen-ion density (pH) in the range of 5-8.

[Claim 14] (I) Art of the substrate according to claim 13 characterized by being the exfoliation liquid for resists with which the exfoliation liquid of a process contains the (a) component 0.2 the (b) component 30 - 5 - 50 % of the weight of 90-% of the weight and (c) components 10% of the weight.

[Claim 15] (I) Art of the substrate according to claim 13 or 14 characterized by for the  
(a) component in the exfoliation liquid of a process being ammonium fluoride, and the  
(b) component being dimethyl sulfoxide.

## DETAILED DESCRIPTION

### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the art of the substrate using the rinse constituent for lithography for [ which carried out exfoliation processing of the rinse constituent for lithography, and the substrate used in the case of semiconductor devices such as IC and LSI, or liquid crystal panel component creation in more detail ] carrying out after rinse processing, and this rinse constituent for lithography.

[0002]

[Description of the Prior Art] Conventionally semiconductor devices and liquid crystal panel components, such as IC and LSI A photoresist is applied to homogeneity on insulator layers, such as conductive metal membranes, such as aluminum formed on the substrate, copper, and an aluminium alloy, and SiO<sub>2</sub> film. After developing negatives, forming a resist pattern, after drawing it with exposure or an electron ray, etching said conductive metal membrane and insulator layer alternatively by using this pattern as a mask and forming a detailed circuit, exfoliation liquid removes an unnecessary resist layer and it is manufactured.

[0003] The organic amine system exfoliation liquid which used as the major component organic amines which used alkylbenzene sulfonic acid as the major component, such as organic sulfonic-acid system exfoliation liquid and monoethanolamine, as exfoliation liquid from which the above-mentioned resist is removed, the fluoric acid system exfoliation liquid which used the hydrofluoric acid as the major component are mentioned. It has the fault that said organic sulfonic-acid system exfoliation liquid has the place where organic solvents, such as a phenolic compound with high toxicity and a chlorobenzene, are used together to bad workability, and an environmental problem occurs upwards and the conductive metal membrane of a substrate etc. is easy to be corroded. Moreover, organic amine system exfoliation liquid has low toxicity compared with organic sulfonic-acid system exfoliation liquid. Although complicated processing is not required for waste fluid processing and the corrosion prevention effectiveness of a substrate that the detachability of the deterioration film formed by processing of dry ECHINGU, ashing, an ion implantation, etc. contains aluminum, Cu, etc. in a good top is excellent The detachability of the resist film which deteriorated even in the inorganic

property is not enough, and since processing temperature is an elevated temperature comparatively with 60-130 degrees C, the inflammable organic compound in exfoliation liquid volatilizes, since there is a danger of igniting to it, a large amount of disaster prevention facilities are needed, and it has a fault, such as becoming cost quantity. still more complicated exhaust-air processing and waste-fluid processing are [ that it tends to corrode peripheral devices, such as a drug solution feeder which connects the container containing exfoliation liquid to an exfoliation tub, from the place where a problem is in the safety to the body at, it is hard to deal with it upwards at, and a constituent serves as acidity although the fluoric-acid system exfoliation liquid which furthermore uses a hydrofluoric acid as a major component is excellent in the detachability of said inorganic deterioration film ] required — etc. — there is a trouble.

[0004]

[Problem(s) to be Solved by the Invention] As exfoliation liquid which solves many above-mentioned troubles, this invention person etc. has already proposed the exfoliation liquid (henceforth hydrofluoric-acid salt system exfoliation liquid) which used as the major component the salt of a hydrofluoric acid and the base which does not contain a metal. Although exfoliation processing at low temperature can perform said hydrofluoric-acid salt system exfoliation liquid upwards in a short time, and it can prevent the corrosion of the metal thin film on a substrate, a peripheral device, etc., and its toxicity is low and it has the advantage which can perform exhaust-air processing and waste-fluid processing easily, when the washing time amount in the pure-water washing process after exfoliation processing exceeds for about 10 minutes, there is a difficulty which corrodes metal thin films, such as Ti, aluminum, aluminum-Si, and aluminum-Si-Cu. Although said corrosion thought that it originated in a hydrofluoric acid arising because a hydrofluoric-acid salt contacts water, replaced pure water with organic solvents, such as a methanol, ethanol, isopropyl alcohol, and an acetone, and performed rinse processing, the crystal of a hydrofluoric-acid salt deposited on the substrate conversely, and it was not desirable.

[0005] As a result of this invention person's etc. repeating research wholeheartedly in view of such the present condition, a header and this invention are completed for the burden which can prevent the corrosion of a metal thin film upwards by using as the constituent containing a water-soluble organic solvent and water the rinse constituent for carrying out rinse processing of the substrate which carried out exfoliation processing with hydrofluoric-acid salt system exfoliation liquid, and starts waste fluid processing of the pure-water penetrant remover after rinse processing being mitigable. Namely, [0006] This invention aims at offering the rinse constituent for lithography

which does not corrode the metal thin film of a substrate.

[0007] Moreover, this invention aims at offering the art of a substrate which uses this rinse constituent for lithography.

[0008]

[Means for Solving the Problem] This invention which attains the above-mentioned purpose relates to the art of the substrate using the rinse constituent for lithography characterized by being a rinse constituent for carrying out rinse processing of the substrate which processed the salt of a hydrofluoric acid and the base which does not contain a metal with the exfoliation liquid used as a major component, and being the constituent with which said rinse constituent contains a water-soluble organic solvent and water, and this rinse constituent for lithography.

[0009] The rinse constituent for lithography of this invention is a rinse for carrying out rinse processing of the semiconductor device which carried out exfoliation processing with hydrofluoric-acid salt system exfoliation liquid, or the substrate for liquid crystal panel component manufacture, and is a constituent containing a water-soluble organic solvent and water. As said water-soluble organic solvent, methyl alcohol, ethyl alcohol, Sulfoxides, such as alcohols of monovalence, such as isopropyl alcohol, and dimethyl sulfoxide A dimethyl sulfone, diethyl sulfone, a bis(2-hydroxyethyl) sulfone, Sulfones, such as a tetramethylen sulfone, N,N-dimethylformamide, N-methyl formamide, N,N-dimethylacetamide, N-methyl acetamide, Amides, such as N and N-diethyl acetamide, a N-methyl-2-pyrrolidone, An N-ethyl-2-pyrrolidone, an N-propyl-2-pyrrolidone, an N-hydroxymethyl-2-pyrrolidone, Lactams, such as an N-hydroxyethyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, Imidazolidinone, such as 1, 3-diethyl-2-imidazolidinone, 1, and 3-diisopropyl-2-imidazolidinone Lactone, such as gamma-butyrolactone and delta-valerolactone, ethylene glycol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, Polyhydric alcohol, such as ethylene glycol monoethyl ether acetate, a diethylene glycol, the diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, and the diethylene-glycol monobutyl ether, and the derivative of those are mentioned. Although methyl alcohol, ethyl alcohol, isopropyl alcohol, dimethyl sulfoxide, N.N-dimethylformamide, N,N-dimethylacetamide, a N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, ethylene glycol, and the diethylene-glycol monobutyl ether are desirable in these, processing with the alcohol of monovalence, such as methyl alcohol, ethyl alcohol, and isopropyl alcohol, especially complicated at the time of waste fluid processing of a rinse can be unnecessary, can be processed cheaply, and is desirable.

[0010] The rinse constituent for lithography of this invention contains the water-soluble above-mentioned organic solvent in 20 - 60% of the weight of the range preferably 10 - 80 % of the weight of water 40 to 80% of the weight 20 to 90% of the weight. If are easy to deposit and there are few crystals of a hydrofluoric-acid salt on a substrate when there are more water-soluble organic solvents than said range, the corrosion of a metal thin film happens and is not desirable.

[0011] In addition to the above-mentioned component, the rinse constituent for lithography of this invention can contain anticorrosives. As said anticorrosives, an aromatic series hydroxy compound, acetylene alcohol, a carboxyl group content organic compound and its anhydride, a triazole compound, and a saccharide are mentioned. As an aromatic series hydroxy compound, concretely A phenol, cresol, A xylenol, a pyrocatechol, resorcinol, a hydroquinone, pyrogallol, 1, 2, 4-benzene triol, salicyl alcohol, p-hydroxybenzyl alcohol, Ortho hydroxybenzyl alcohol, p-hydroxy phenethyl alcohol, Para aminophenol, m-aminophenol, diaminophenol, Amino resorcinol, para hydroxybenzoic acid, o-hydroxybenzoic acid, 2, 4-dihydroxybenzoic acid, 2, 5-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3, and 5-dihydroxybenzoic acid etc. can be mentioned, and a pyrocatechol is suitable especially.

[0012] As acetylene alcohol, 2-butine -1, 4-diol, 3,5-dimethyl-1-hexyn-3-ol, 2-methyl-3-butyne-2-oar, 3-methyl-1-pentyn-3-ol, 3, the 6-dimethyl-4-octyne -3, 6-diol, 2,4,7,9-tetra-methyl-5-decyne-4,7-diol, 2,5-dimethyl-3-hexyne-2,5-diol, etc. can be mentioned concretely. 2-butine -1 and 4-diol are suitable especially.

[0013] As a carboxyl group content organic compound and its anhydride, they are formic acid, an acetic acid, a propionic acid, butanoic acid, an isobutyric acid, oxalic acid, a malonic acid, a succinic acid, a glutaric acid, a maleic acid, a fumaric acid, a benzoic acid, a phthalic acid, 1 and 2, 3-benzene tricarboxylic acid, a glycolic acid, a lactic acid, a malic acid, and a citric acid. An acetic anhydride, phthalic anhydride, a maleic anhydride, a succinic anhydride, a salicylic acid, etc. can be mentioned. As a desirable carboxyl group content organic compound, there are formic acid, a phthalic acid, a benzoic acid, phthalic anhydride, and a salicylic acid, and especially a phthalic acid, phthalic anhydride, and a salicylic acid are suitable.

[0014] As a triazole compound, benzotriazol, o-tolyl triazole, m-tolyl triazole, p-tolyl triazole, carboxy benzotriazol, 1-hydroxy benzotriazol, nitrobenzo triazole, dihydroxy propyl benzotriazol, etc. can be mentioned, and benzotriazol is suitable especially.

[0015] As a saccharide, D-sorbitol, arabitol, a mannitol, sucrose, starch, etc. can be mentioned concretely, and D-sorbitol is suitable especially.

[0016] Even if each above-mentioned anticorrosives are independent, and even if they

combine two or more sorts, they can be used.

[0017] The rinse constituent for lithography of this invention containing the above-mentioned anticorrosives has the good range of 55 - 85 % of the weight of water-soluble organic solvents, 10 - 40 % of the weight of water, and 0.5 - 15 % of the weight of anticorrosives. The corrosion of a metal thin film can control much more by containing the anticorrosives of said range, and it is suitable.

[0018] Although it will not be limited especially if the above-mentioned hydrofluoric-acid salt system exfoliation liquid is exfoliation liquid which uses as a major component the base of the (a) hydrofluoric acid and the base which does not contain a metal and it is the exfoliation liquid which uses a \*\* (a) component as main components, the almost neutral exfoliation liquid for resists which contains the aforementioned (a) component, (b) water solubility organic solvent, and (c) water, and has a hydrogen-ion density (pH) in the range of 5-8 is suitable. The base which does not contain a metal in a molecule as a base which does not contain said metal like organic amines, such as fatty amine of hydroxylamines, the 1st class, the 2nd class, or the 3rd class, an alicyclic amine, aromatic amine, and heterocyclic amine, aqueous ammonia, or a low-grade alkyl quarternary-ammonium-salt radical is said. As said hydroxylamines, hydroxylamine, N, and N-diethylhydroxylamine etc. concretely as the 1st class fatty amine Monoethanolamine, ethylenediamine, 2-(2-aminoethyl amino) ethanol, etc. concretely as the 2nd class fatty amine Diethanolamine, a dipropyl amine, 2-ethylamino ethanol, etc. concretely as fatty amine of the 3rd class Dimethylamino ethanol, ethyl diethanolamine, etc. concretely as an alicyclic amine Cyclohexylamine, dicyclohexylamine, etc. concretely as aromatic amine Benzylamine, dibenzylamine, N-methylbenzyl amine, etc. concretely as heterocyclic amine A pyrrole, a pyrrolidine, a pyrrolidone, a pyridine, a morpholine, pyrazine, a piperidine, N-hydroxyethyl piperidine, oxazole, a thiazole, etc. are mentioned concretely. Furthermore as a low-grade alkyl quarternary-ammonium-salt radical, tetramethylammonium hydroxide, TORIMECHIRU (2-hydroxyethyl) ammonium hydroxide (choline), etc. are mentioned concretely. Aqueous ammonia, monoethanolamine, and tetramethylammonium hydroxide are desirable especially from the place acquisition excels [ place ] in safety in the easy top. The salt of the base and hydrofluoric acid which do not contain said metal can be manufactured by adding the base which does not contain a metal in the hydrofluoric acid of commercial 50 - 60% concentration of hydrogen fluoride so that pH may be set to 5-8. It cannot be overemphasized that commercial ammonium fluoride can be used as said salt. pH of said hydrofluoric-acid salt system exfoliation liquid constituent cannot be uniquely specified from the place where the contents for making it

neutrality according to the class of base which does not contain the metal of 5-8 added to a hydrofluoric acid differ, although what is necessary is just to prepare the (a) component neutrally mostly for making it neutrality mostly. For example, in the case of aqueous ammonia, if isochore product mixing of the hydrofluoric acid and aqueous ammonia of equimolar concentration is carried out, the (a) component of pH made into the purpose can be prepared. Moreover, in the case of ethanolamine, if one mol of monoethanolamines is mixed with 1000ml of one mol [l.] hydrofluoric acids, the (a) component can be prepared similarly. (a) When the pH value of a component is in said range, there is no fall of the detachability of the deterioration film, the corrosion of peripheral devices, such as a metal membrane on a substrate and a drug solution feeder, can be controlled, and it can be dealt with safely. Furthermore, it needs the complicated exhaust air processing and waste fluid processing which originate in generating of said hydrogen fluoride from a place with few contents of hydrogen fluoride and is suitable.

[0019] As a (b) component of the above-mentioned hydrofluoric-acid salt system exfoliation liquid constituent, the water-soluble organic solvent of the above-mentioned rinse constituent for lithography and the same water-soluble organic solvent can be used. Dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, a N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, ethylene glycol, and the diethylene-glycol monobutyl ether excel in the detachability of the resist deterioration film and are desirable also in this water-soluble organic solvent. Especially, dimethyl sulfoxide is desirable. Moreover, when the (b) component is used as the water-soluble organic solvent containing at least 10% of the weight of ethylene glycol, the corrosion prevention effectiveness of a metal vacuum evaporationo plate is high at the time of exfoliation processing of a hole-like resist pattern, and desirable to it. Under the present circumstances, since the corrosion prevention effectiveness improves so that there are many contents of ethylene glycol, it is [ an ethylene glycol independent ] good also as a (b) component, and it is good also as dimethyl sulfoxide and mixture of same weight.

[0020] The 0.5 - (b) component has [ 90 % of the weight and 5 - 50 % of the weight of 40 - (c) components ] 20 - 40% of the weight of the range preferably good [ the component rate of the above-mentioned hydrofluoric-acid salt system exfoliation liquid / the (a) component ] 10% of the weight 0.2 to 10% of the weight preferably 30 to 90% of the weight. When each component contains in said range, the detachability of the deterioration film, the detachability in a room temperature, and the corrosion prevention effectiveness of a substrate improve. In the case of substrates, such as the substrate of metal vacuum evaporationo with which the substrate which exfoliates especially is easy to be corroded, for example, aluminum, aluminum-Si, and aluminum-Si-Cu, it makes it

indispensable to consider as said range. (a) When there are few components than said range, the detachability of the deterioration film falls, and in many, it becomes easy to corrode a substrate.

[0021] Furthermore, the above-mentioned hydrofluoric-acid salt system exfoliation liquid can contain (d) anticorrosives. (d) As a component, the same thing as the anticorrosives of the above-mentioned rinse constituent for lithography can be used. Anti-corrosiveness can be improved much more, without falling the detachability of the deterioration film of substrates, such as aluminum, aluminum-Si, and aluminum-Si-Cu, by containing the aforementioned (d) component.

[0022] 1 - 30% of the weight of the range is preferably suitable [ the component rate of the hydrofluoric-acid salt system exfoliation liquid containing the above-mentioned (d) component / 0.5 - 10-% of the weight and (b) component / 30 to 80% of the weight / 40 - 70-% of the weight and (c) component ] for the (a) component 0.2 to 10 weight for 20 - 40-% of the weight and (d) component preferably 0.5 to 40% of the weight five to 50% of the weight. When each component deviates from said range, it is inferior to the detachability of the deterioration film, and anti-corrosiveness.

[0023] After the art of the substrate of this invention prepares a desired resist pattern on a substrate and carries out etching processing, it consists of the process which processes a salt with the base which does not contain a hydrofluoric acid and a metal for the (I) resist pattern with the exfoliation liquid constituent used as a major component, a process which carries out rinse processing of the (II) substrate with the rinse constituent for lithography containing a water-soluble organic solvent and water, and (III) a process which carries out washing processing with water. The process which prepares said resist pattern is good by the pattern formation approach usually performed. The resist constituent of a positive type or a negative mold to substrates used in the case of a semiconductor device or liquid crystal panel component creation, such as a silicon wafer and a glass substrate, for example, the rotation applying method, A resist layer is formed using the applying methods, such as the roll coater method and the bar coating-machine method. Subsequently, by irradiating or drawing radiations, such as ultraviolet rays, far ultraviolet rays containing an excimer laser, an electron ray, and an X-ray, through a mask pattern, a latent image is formed, negatives are developed in an alkali water solution, and there is the approach of forming a resist pattern etc. What is necessary is to be a room temperature and just to process for 1 - 20 minutes by dip coating etc., in said exfoliation processing. Moreover, what is necessary is to be a room temperature and just to process for 3 - 20 minutes by dip coating etc., in rinse processing. Although direct washing processing was performed without rinse processing

in the conventional exfoliation approach Although fluorine ion and a fluoride increased to the cleaning tank and complicated processing was needed for waste fluid processing at the process washed with the water of a repeat mass Since neither fluorine ion nor a fluoride remains in a cleaning tank in order to carry out rinse processing before washing processing in the art of the substrate of this invention, the burden placed on the waste fluid processing in a cleaning tank is required by mitigation, and there is an advantage which continues and can perform exfoliation processing, rinse processing, and washing processing efficiently upwards.

[0024]

[The mode of implementation of invention] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0025]

[Example]

examples 1-6 — on the silicon wafer which vapor-deposited about 1.0-micrometer aluminum-Si-Cu film, spinner spreading of THMR-iP3300 (TOKYO OHKA KOGYO CO., LTD. make) which is the positive type photoresist which consists of a naphthoquinonediazide compound and novolak resin was carried out, at 90 degrees C, prebake for 90 seconds was given and the resist layer of 2.0 micrometers of thickness was formed. This resist layer was exposed through the mask pattern using NSR-2005i10D (NIKON CORP. make), negatives were developed in 2.38% of the weight of the tetramethylammonium hydroxide water solution, and the resist pattern was formed. Subsequently, postbake for 90 seconds was performed at 120 degrees C.

[0026] Next, etching processing of the silicon wafer which vapor-deposited about 1.0-micrometer aluminum-Si-Cu film which has the above-mentioned resist pattern was carried out for 168 seconds at pressure 5mmTorr and the stage temperature of 20 degrees C by having made the mixed gas of chlorine and boron trichloride into etchant using etching system TSS-6000 (TOKYO OHKA KOGYO CO., LTD. make), and, subsequently after corrosion processing was carried out for 30 seconds at pressure 20mmTorr and the stage temperature of 20 degrees C using oxygen and the mixed gas of trifluoromethane. By ashing device TCA-2400 (TOKYO OHKA KOGYO CO., LTD. make), conditions with a pressure 0.3mmTorr and a stage temperature of 60 degrees C performed ashing processing for 150 seconds using oxygen gas further after said processing.

[0027] The above-mentioned processed silicon wafer was immersed in 1.0 % of the weight of ammonium fluoride salts, 69.0 % of the weight of dimethyl sulfoxide, and exfoliation liquid of 30 % of the weight of water for 5 minutes at 23 degrees C, and

exfoliation processing was performed. The corroded condition of the substrate after carrying out rinse processing and carrying out pure-water washing further by the rinse of the presentation which shows the processed substrate in Table 1 was observed. The result is shown in Table 1.

[0028] In example of comparison 1 example 1, corrosive evaluation was performed like the example except having replaced the presentation of a rinse only with water. The result is shown in Table 1.

[0029]

[Table 1]

	リシス液組成	23℃で20分水に浸漬 後の腐食状態
実施例1	メタノール：水 (50:50)	○
実施例2	メタノール：水 (80:20)	○
実施例3	エタノール：水 (70:30)	○
実施例4	エタノール：水 (30:70)	○
実施例5	イソプロピルアルコール：水 (70:30)	○
実施例6	イソプロピルアルコール：水 (50:50)	○
比較例1	水	×

Notes corroded-condition O: With no corrosion x: Those with corrosion [0030]

[Effect of the Invention] Corrosion does not take place to metal thin films which are easy to be corroded by using the rinse constituent for lithography of this invention, such as aluminum, aluminum-Si, and aluminum-Si-Cu. Moreover, if it is in the art of the substrate using the rinse constituent for lithography of this invention, the waste water treatment after [ the place where fluorine ion remains for carrying out little content extremely to ] pure-water washing processing is unnecessary to the pure-water penetrant remover after rinse processing, and can perform efficiently exfoliation processing, rinse processing, and washing processing to it continuously.

## TECHNICAL FIELD

[Industrial Application] This invention relates to the art of the substrate using the rinse constituent for lithography for [ which carried out exfoliation processing of the rinse constituent for lithography, and the substrate used in the case of semiconductor devices

such as IC and LSI, or liquid crystal panel component creation in more detail ] carrying out after rinse processing, and this rinse constituent for lithography.

## PRIOR ART

[Description of the Prior Art] Conventionally semiconductor devices and liquid crystal panel components, such as IC and LSI A photoresist is applied to homogeneity on insulator layers, such as conductive metal membranes, such as aluminum formed on the substrate, copper, and an aluminium alloy, and SiO<sub>2</sub> film. After developing negatives, forming a resist pattern, after drawing it with exposure or an electron ray, etching said conductive metal membrane and insulator layer alternatively by using this pattern as a mask and forming a detailed circuit, exfoliation liquid removes an unnecessary resist layer and it is manufactured.

[0003] The organic amine system exfoliation liquid which used as the major component organic amines which used alkylbenzene sulfonic acid as the major component, such as organic sulfonic-acid system exfoliation liquid and monoethanolamine, as exfoliation liquid from which the above-mentioned resist is removed, the fluoric acid system exfoliation liquid which used the hydrofluoric acid as the major component are mentioned. It has the fault that said organic sulfonic-acid system exfoliation liquid has the place where organic solvents, such as a phenolic compound with high toxicity and a chlorobenzene, are used together to bad workability, and an environmental problem occurs upwards and the conductive metal membrane of a substrate etc. is easy to be corroded. Moreover, organic amine system exfoliation liquid has low toxicity compared with organic sulfonic-acid system exfoliation liquid. Although complicated processing is not required for waste fluid processing and the corrosion prevention effectiveness of a substrate that the detachability of the deterioration film formed by processing of dry ECHINGU, ashing, an ion implantation, etc. contains aluminum, Cu, etc. in a good top is excellent The detachability of the resist film which deteriorated even in the inorganic property is not enough, and since processing temperature is an elevated temperature comparatively with 60-130 degrees C, the inflammable organic compound in exfoliation liquid volatilizes, since there is a danger of igniting to it, a large amount of disaster prevention facilities are needed, and it has a fault, such as becoming cost quantity. still more complicated exhaust-air processing and waste-fluid processing are [ that it tends to corrode peripheral devices, such as a drug solution feeder which connects the container containing exfoliation liquid to an exfoliation tub, from the place where a problem is in the safety to the body at, it is hard to deal with it upwards at, and a constituent serves as acidity although the fluoric-acid system exfoliation liquid which furthermore uses a

hydrofluoric acid as a major component is excellent in the detachability of said inorganic deterioration film ] required — etc. — there is a trouble.

## **EFFECT OF THE INVENTION**

[Effect of the Invention] Corrosion does not take place to metal thin films which are easy to be corroded by using the rinse constituent for lithography of this invention, such as aluminum, aluminum-Si, and aluminum-Si-Cu. Moreover, if it is in the art of the substrate using the rinse constituent for lithography of this invention, the waste water treatment after [ the place where fluorine ion remains for carrying out little content extremely to ] pure-water washing processing is unnecessary to the pure-water penetrant remover after rinse processing, and can perform efficiently exfoliation processing, rinse processing, and washing processing to it continuously.

## **TECHNICAL PROBLEM**

[Problem(s) to be Solved by the Invention] As exfoliation liquid which solves many above-mentioned troubles, this invention person etc. has already proposed the exfoliation liquid (henceforth hydrofluoric-acid salt system exfoliation liquid) which used as the major component the salt of a hydrofluoric acid and the base which does not contain a metal. Although exfoliation processing at low temperature can perform said hydrofluoric-acid salt system exfoliation liquid upwards in a short time, and it can prevent the corrosion of the metal thin film on a substrate, a peripheral device, etc., and its toxicity is low and it has the advantage which can perform exhaust-air processing and waste-fluid processing easily, when the washing time amount in the pure-water washing process after exfoliation processing exceeds for about 10 minutes, there is a difficulty which corrodes metal thin films, such as Ti, aluminum, aluminum-Si, and aluminum-Si-Cu. Although said corrosion thought that it originated in a hydrofluoric acid arising because a hydrofluoric-acid salt contacts water, replaced pure water with organic solvents, such as a methanol, ethanol, isopropyl alcohol, and an acetone, and performed rinse processing, the crystal of a hydrofluoric-acid salt deposited on the substrate conversely, and it was not desirable.

[0005] As a result of this invention person's etc. repeating research wholeheartedly in view of such the present condition, a header and this invention are completed for the burden which can prevent the corrosion of a metal thin film upwards by using as the constituent containing a water-soluble organic solvent and water the rinse constituent for carrying out rinse processing of the substrate which carried out exfoliation processing with hydrofluoric-acid salt system exfoliation liquid, and starts waste fluid

processing of the pure-water penetrant remover after rinse processing being mitigable. Namely, [0006] This invention aims at offering the rinse constituent for lithography which does not corrode the metal thin film of a substrate.

[0007] Moreover, this invention aims at offering the art of a substrate which uses this rinse constituent for lithography.

## MEANS

[Means for Solving the Problem] This invention which attains the above-mentioned purpose relates to the art of the substrate using the rinse constituent for lithography characterized by being a rinse constituent for carrying out rinse processing of the substrate which processed the salt of a hydrofluoric acid and the base which does not contain a metal with the exfoliation liquid used as a major component, and being the constituent with which said rinse constituent contains a water-soluble organic solvent and water, and this rinse constituent for lithography.

[0009] The rinse constituent for lithography of this invention is a rinse for carrying out rinse processing of the semiconductor device which carried out exfoliation processing with hydrofluoric-acid salt system exfoliation liquid, or the substrate for liquid crystal panel component manufacture, and is a constituent containing a water-soluble organic solvent and water. As said water-soluble organic solvent, methyl alcohol, ethyl alcohol, Sulfoxides, such as alcohols of monovalence, such as isopropyl alcohol, and dimethyl sulfoxide A dimethyl sulfone, diethyl sulfone, a bis(2-hydroxyethyl) sulfone, Sulfones, such as a tetramethylen sulfone, N,N-dimethylformamide, N-methyl formamide, N,N-dimethylacetamide, N-methyl acetamide, Amides, such as N and N-diethyl acetamide, a N-methyl-2-pyrrolidone, An N-ethyl-2-pyrrolidone, an N-propyl-2-pyrrolidone, an N-hydroxymethyl-2-pyrrolidone, Lactams, such as an N-hydroxyethyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, Imidazolidinone, such as 1, 3-diethyl-2-imidazolidinone, 1, and 3-diisopropyl-2-imidazolidinone Lactone, such as gamma-butyrolactone and delta-valerolactone, ethylene glycol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, Polyhydric alcohol, such as ethylene glycol monoethyl ether acetate, a diethylene glycol, the diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, and the diethylene-glycol monobutyl ether, and the derivative of those are mentioned. Although methyl alcohol, ethyl alcohol, isopropyl alcohol, dimethyl sulfoxide, N.N-dimethylformamide, N,N-dimethylacetamide, a N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, ethylene glycol, and the diethylene-glycol monobutyl ether are desirable in these, processing with the alcohol of

monovalence, such as methyl alcohol, ethyl alcohol, and isopropyl alcohol, especially complicated at the time of waste fluid processing of a rinse can be unnecessary, can be processed cheaply, and is desirable.

[0010] The rinse constituent for lithography of this invention contains the water-soluble above-mentioned organic solvent in 20 - 60% of the weight of the range preferably 10 - 80 % of the weight of water 40 to 80% of the weight 20 to 90% of the weight. If are easy to deposit and there are few crystals of a hydrofluoric-acid salt on a substrate when there are more water-soluble organic solvents than said range, the corrosion of a metal thin film happens and is not desirable.

[0011] In addition to the above-mentioned component, the rinse constituent for lithography of this invention can contain anticorrosives. As said anticorrosives, an aromatic series hydroxy compound, acetylene alcohol, a carboxyl group content organic compound and its anhydride, a triazole compound, and a saccharide are mentioned. As an aromatic series hydroxy compound, concretely A phenol, cresol, A xylenol, a pyrocatechol, resorcinol, a hydroquinone, pyrogallol, 1, 2, 4-benzene triol, salicyl alcohol, p-hydroxybenzyl alcohol, Ortho hydroxybenzyl alcohol, p-hydroxy phenethyl alcohol, Para aminophenol, m-aminophenol, diaminophenol, Amino resorcinol, para hydroxybenzoic acid, o-hydroxybenzoic acid, 2, 4-dihydroxybenzoic acid, 2, 5-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3, and 5-dihydroxybenzoic acid etc. can be mentioned, and a pyrocatechol is suitable especially.

[0012] As acetylene alcohol, 2-butine -1, 4-diol, 3,5-dimethyl-1-hexyn-3-ol, 2-methyl-3-butyne-2-oar, 3-methyl-1-pentyn-3-ol, 3, the 6-dimethyl-4-octyne -3, 6-diol, 2,4,7,9-tetra-methyl-5-decyne-4,7-diol, 2,5-dimethyl-3-hexyne-2,5-diol, etc. can be mentioned concretely. 2-butine -1 and 4-diol are suitable especially.

[0013] As a carboxyl group content organic compound and its anhydride, they are formic acid, an acetic acid, a propionic acid, butanoic acid, an isobutyric acid, oxalic acid, a malonic acid, a succinic acid, a glutaric acid, a maleic acid, a fumaric acid, a benzoic acid, a phthalic acid, 1 and 2, 3-benzene tricarboxylic acid, a glycolic acid, a lactic acid, a malic acid, and a citric acid. An acetic anhydride, phthalic anhydride, a maleic anhydride, a succinic anhydride, a salicylic acid, etc. can be mentioned. As a desirable carboxyl group content organic compound, there are formic acid, a phthalic acid, a benzoic acid, phthalic anhydride, and a salicylic acid, and especially a phthalic acid, phthalic anhydride, and a salicylic acid are suitable.

[0014] As a triazole compound, benzotriazol, o-tolyl triazole, m-tolyl triazole, p-tolyl triazole, carboxy benzotriazol, 1-hydroxy benzotriazol, nitrobenzo triazole, dihydroxy propyl benzotriazol, etc. can be mentioned, and benzotriazol is suitable especially.

[0015] As a saccharide, D-sorbitol, arabitol, a mannitol, sucrose, starch, etc. can be mentioned concretely, and D-sorbitol is suitable especially.

[0016] Even if each above-mentioned anticorrosives are independent, and even if they combine two or more sorts, they can be used.

[0017] The rinse constituent for lithography of this invention containing the above-mentioned anticorrosives has the good range of 55 - 85 % of the weight of water-soluble organic solvents, 10 - 40 % of the weight of water, and 0.5 - 15 % of the weight of anticorrosives. The corrosion of a metal thin film can control much more by containing the anticorrosives of said range, and it is suitable.

[0018] Although it will not be limited especially if the above-mentioned hydrofluoric-acid salt system exfoliation liquid is exfoliation liquid which uses as a major component the base of the (a) hydrofluoric acid and the base which does not contain a metal and it is the exfoliation liquid which uses a \*\* (a) component as main components, the almost neutral exfoliation liquid for resists which contains the aforementioned (a) component, (b) water solubility organic solvent, and (c) water, and has a hydrogen-ion density (pH) in the range of 5-8 is suitable. The base which does not contain a metal in a molecule as a base which does not contain said metal like organic amines, such as fatty amine of hydroxylamines, the 1st class, the 2nd class, or the 3rd class, an alicyclic amine, aromatic amine, and heterocyclic amine, aqueous ammonia, or a low-grade alkyl quarternary-ammonium-salt radical is said. As said hydroxylamines, hydroxylamine, N, and N-diethylhydroxylamine etc. concretely as the 1st class fatty amine Monoethanolamine, ethylenediamine, 2-(2-aminoethyl amino) ethanol, etc. concretely as the 2nd class fatty amine Diethanolamine, a dipropyl amine, 2-ethylamino ethanol, etc. concretely as fatty amine of the 3rd class Dimethylamino ethanol, ethyl diethanolamine, etc. concretely as an alicyclic amine Cyclohexylamine, dicyclohexylamine, etc. concretely as aromatic amine Benzylamine, dibenzylamine, N-methylbenzyl amine, etc. concretely as heterocyclic amine A pyrrole, a pyrrolidine, a pyrrolidone, a pyridine, a morpholine, pyrazine, a piperidine, N-hydroxyethyl piperidine, oxazole, a thiazole, etc. are mentioned concretely. Furthermore as a low-grade alkyl quarternary-ammonium-salt radical, tetramethylammonium hydroxide, TORIMECHIRU (2-hydroxyethyl) ammonium hydroxide (choline), etc. are mentioned concretely. Aqueous ammonia, monoethanolamine, and tetramethylammonium hydroxide are desirable especially from the place acquisition excels [ place ] in safety in the easy top. The salt of the base and hydrofluoric acid which do not contain said metal can be manufactured by adding the base which does not contain a metal in the hydrofluoric acid of commercial 50 - 60% concentration of hydrogen fluoride so that

pH may be set to 5-8. It cannot be overemphasized that commercial ammonium fluoride can be used as said salt. pH of said hydrofluoric-acid salt system exfoliation liquid constituent cannot be uniquely specified from the place where the contents for making it neutrality according to the class of base which does not contain the metal of 5-8 added to a hydrofluoric acid differ, although what is necessary is just to prepare the (a) component neutrally mostly for making it neutrality mostly. For example, in the case of aqueous ammonia, if isochore product mixing of the hydrofluoric acid and aqueous ammonia of equimolar concentration is carried out, the (a) component of pH made into the purpose can be prepared. Moreover, in the case of ethanolamine, if one mol of monoethanolamines is mixed with 1000ml of one mol [1.] hydrofluoric acids, the (a) component can be prepared similarly. (a) When the pH value of a component is in said range, there is no fall of the detachability of the deterioration film, the corrosion of peripheral devices, such as a metal membrane on a substrate and a drug solution feeder, can be controlled, and it can be dealt with safely. Furthermore, it needs the complicated exhaust air processing and waste fluid processing which originate in generating of said hydrogen fluoride from a place with few contents of hydrogen fluoride and is suitable.

[0019] As a (b) component of the above-mentioned hydrofluoric-acid salt system exfoliation liquid constituent, the water-soluble organic solvent of the above-mentioned rinse constituent for lithography and the same water-soluble organic solvent can be used. Dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, a N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, ethylene glycol, and the diethylene-glycol monobutyl ether excel in the detachability of the resist deterioration film and are desirable also in this water-soluble organic solvent. Especially, dimethyl sulfoxide is desirable. Moreover, when the (b) component is used as the water-soluble organic solvent containing at least 10% of the weight of ethylene glycol, the corrosion prevention effectiveness of a metal vacuum evaporationo plate is high at the time of exfoliation processing of a hole-like resist pattern, and desirable to it. Under the present circumstances, since the corrosion prevention effectiveness improves so that there are many contents of ethylene glycol, it is [ an ethylene glycol independent ] good also as a (b) component, and it is good also as dimethyl sulfoxide and mixture of same weight.

[0020] The 0.5 - (b) component has [ 90 % of the weight and 5 - 50 % of the weight of 40 - (c) components ] 20 - 40% of the weight of the range preferably good [ the component rate of the above-mentioned hydrofluoric-acid salt system exfoliation liquid / the (a) component ] 10% of the weight 0.2 to 10% of the weight preferably 30 to 90% of the weight. When each component contains in said range, the detachability of the deterioration film, the detachability in a room temperature, and the corrosion prevention

effectiveness of a substrate improve. In the case of substrates, such as the substrate of metal vacuum evaporationo with which the substrate which exfoliates especially is easy to be corroded, for example, aluminum, aluminum-Si, and aluminum-Si-Cu, it makes it indispensable to consider as said range. (a) When there are few components than said range, the detachability of the deterioration film falls, and in many, it becomes easy to corrode a substrate.

[0021] Furthermore, the above-mentioned hydrofluoric-acid salt system exfoliation liquid can contain (d) anticorrosives. (d) As a component, the same thing as the anticorrosives of the above-mentioned rinse constituent for lithography can be used. Anti-corrosiveness can be improved much more, without falling the detachability of the deterioration film of substrates, such as aluminum, aluminum-Si, and aluminum-Si-Cu, by containing the aforementioned (d) component.

[0022] 1 - 30% of the weight of the range is preferably suitable [ the component rate of the hydrofluoric-acid salt system exfoliation liquid containing the above-mentioned (d) component / 0.5 - 10-% of the weight and (b) component / 30 to 80% of the weight / 40 - 70-% of the weight and (c) component ] for the (a) component 0.2 to 10 weight for 20 - 40-% of the weight and (d) component preferably 0.5 to 40% of the weight five to 50% of the weight. When each component deviates from said range, it is inferior to the detachability of the deterioration film, and anti-corrosiveness.

[0023] After the art of the substrate of this invention prepares a desired resist pattern on a substrate and carries out etching processing, it consists of the process which processes a salt with the base which does not contain a hydrofluoric acid and a metal for the (I) resist pattern with the exfoliation liquid constituent used as a major component, a process which carries out rinse processing of the (II) substrate with the rinse constituent for lithography containing a water-soluble organic solvent and water, and (III) a process which carries out washing processing with water. The process which prepares said resist pattern is good by the pattern formation approach usually performed. The resist constituent of a positive type or a negative mold to substrates used in the case of a semiconductor device or liquid crystal panel component creation, such as a silicon wafer and a glass substrate, for example, the rotation applying method, A resist layer is formed using the applying methods, such as the roll coater method and the bar coating-machine method. Subsequently, by irradiating or drawing radiations, such as ultraviolet rays, far ultraviolet rays containing an excimer laser, an electron ray, and an X-ray, through a mask pattern, a latent image is formed, negatives are developed in an alkali water solution, and there is the approach of forming a resist pattern etc. What is necessary is to be a room temperature and just to process for 1 - 20 minutes by dip

coating etc., in said exfoliation processing. Moreover, what is necessary is to be a room temperature and just to process for 3 - 20 minutes by dip coating etc., in rinse processing. Although direct washing processing was performed without rinse processing in the conventional exfoliation approach. Although fluorine ion and a fluoride increased to the cleaning tank and complicated processing was needed for waste fluid processing at the process washed with the water of a repeat mass. Since neither fluorine ion nor a fluoride remains in a cleaning tank in order to carry out rinse processing before washing processing in the art of the substrate of this invention, the burden placed on the waste fluid processing in a cleaning tank is required by mitigation, and there is an advantage which continues and can perform exfoliation processing, rinse processing, and washing processing efficiently upwards.

[0024]

[The mode of implementation of invention] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

## **EXAMPLE**

[Example]

examples 1-6 — on the silicon wafer which vapor-deposited about 1.0-micrometer aluminum-Si-Cu film, spinner spreading of THMR-iP3300 (TOKYO OHKA KOGYO CO., LTD. make) which is the positive type photoresist which consists of a naphthoquinonediazide compound and novolak resin was carried out, at 90 degrees C, prebake for 90 seconds was given and the resist layer of 2.0 micrometers of thickness was formed. This resist layer was exposed through the mask pattern using NSR-2005i10D (NIKON CORP. make), negatives were developed in 2.38% of the weight of the tetramethylammonium hydroxide water solution, and the resist pattern was formed. Subsequently, postbake for 90 seconds was performed at 120 degrees C.

[0026] Next, etching processing of the silicon wafer which vapor-deposited about 1.0-micrometer aluminum-Si-Cu film which has the above-mentioned resist pattern was carried out for 168 seconds at pressure 5mmTorr and the stage temperature of 20 degrees C by having made the mixed gas of chlorine and boron trichloride into etchant using etching system TSS-6000 (TOKYO OHKA KOGYO CO., LTD. make), and, subsequently after corrosion processing was carried out for 30 seconds at pressure 20mmTorr and the stage temperature of 20 degrees C using oxygen and the mixed gas of trifluoromethane. By ashing device TCA-2400 (TOKYO OHKA KOGYO CO., LTD. make), conditions with a pressure 0.3mmTorr and a stage temperature of 60 degrees C performed ashing processing for 150 seconds using oxygen gas further after said

processing.

[0027] The above-mentioned processed silicon wafer was immersed in 1.0 % of the weight of ammonium fluoride salts, 69.0 % of the weight of dimethyl sulfoxide, and exfoliation liquid of 30 % of the weight of water for 5 minutes at 23 degrees C, and exfoliation processing was performed. The corroded condition of the substrate after carrying out rinse processing and carrying out pure-water washing further by the rinse of the presentation which shows the processed substrate in Table 1 was observed. The result is shown in Table 1.

[0028] In example of comparison 1 example 1, corrosive evaluation was performed like the example except having replaced the presentation of a rinse only with water. The result is shown in Table 1.

[0029]

[Table 1]

Notes corroded-condition O: With no corrosion x: Those with corrosion

(19) 日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平10-26832

(43) 公開日 平成10年(1998)1月27日

(51) Int. Cl.<sup>6</sup>  
G03F 7/32  
7/42  
H01L 21/027  
21/304  
21/308

識別記号  
501  
341

F I  
G03F 7/32  
7/42  
H01L 21/304  
21/308

501  
341  
E  
G

審査請求 未請求 請求項の数15 FD (全6頁) 最終頁に続く

(21) 出願番号 特願平8-199574

(22) 出願日 平成8年(1996)7月11日

(71) 出願人 000220239  
東京応化工業株式会社  
神奈川県川崎市中原区中丸子150番地  
(72) 発明者 田辺 将人  
神奈川県川崎市中原区中丸子150番地 東  
京応化工業株式会社内  
(72) 発明者 脇屋 和正  
神奈川県川崎市中原区中丸子150番地 東  
京応化工業株式会社内  
(72) 発明者 小林 政一  
神奈川県川崎市中原区中丸子150番地 東  
京応化工業株式会社内  
(74) 代理人 弁理士 服部 平八

最終頁に続く

(54) 【発明の名称】リソグラフィー用リンス液組成物及びそれを用いた基板の処理方法

(57) 【要約】

【課題】Al、Al-Si、Al-Si-Cuなどの金属薄膜に腐食を起こすことのないリソグラフィー用リンス液組成物及びそれを用いた基板の処理方法を提供すること。

【解決手段】フッ化水素酸と金属を含まない塩基との塩を主要成分とする剥離液組成物で処理した基板をリンス処理するためのリンス液組成物において、前記リンス液組成物が水溶性有機溶媒と水とを含有することを特徴とするリソグラフィー用リンス液組成物、及び前記リソグラフィー用リンス液組成物で剥離処理後の基板をリンス処理する方法。

## 【特許請求の範囲】

【請求項1】 フッ化水素酸と金属を含まない塩基との塩を主要成分とする剥離液で処理した基板をリンス処理するためのリンス液組成物であって、前記リンス液組成物が水溶性有機溶媒と水とを含有する組成物であることを特徴とするリソグラフィー用リンス液組成物。

【請求項2】 水溶性有機溶媒がアルコール類、グリコールモノエーテル類及び非プロトン性極性溶媒から選ばれる少なくとも1種であることを特徴とする請求項1記載のリソグラフィー用リンス液組成物。

【請求項3】 アルコール類がメチルアルコール、エチルアルコール、イソプロピルアルコール及びエチレングリコールであることを特徴とする請求項2記載のリソグラフィー用リンス液組成物。

【請求項4】 グリコールモノエーテル類がジエチレングリコールモノブチルエーテルであることを特徴とする請求項2記載のリソグラフィー用リンス液組成物。

【請求項5】 非プロトン性極性溶媒がジメチルスルホキシド、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミド、N-メチル-2-ピロリドン及び1,3-ジメチル-2-イミダゾリジノンであることを特徴とする請求項2記載のリソグラフィー用リンス液組成物。

【請求項6】 請求項1記載のフッ化水素酸と金属を含まない塩基との塩を主要成分とする剥離液が、(a) フッ化水素酸と金属を含まない塩基との塩、(b) ジメチルスルホキシド、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミド、N-メチル-2-ピロリドン、1,3-ジメチル-2-イミダゾリジノン、エチレングリコール及びジエチレングリコールモノブチルエーテルから選ばれる少なくとも1種、並びに(c) 水を含有し、かつその水素イオン濃度(pH)が5~8の範囲にあるレジスト用剥離液であることを特徴とする請求項1記載のリソグラフィー用リンス液組成物。

【請求項7】 請求項1記載のフッ化水素酸と金属を含まない塩基との塩を主要成分とする剥離液が、フッ化アンモニウム0.2~1.0重量%、ジメチルスルホキシド30~90重量%及び水5~50重量%を含有するレジスト用剥離液であることを特徴とする請求項1記載のリソグラフィー用リンス液組成物。

【請求項8】 リンス液組成物が水溶性有機溶媒20~90重量%及び水10~80重量%を含有することを特徴とする請求項1乃至7のいずれかに記載のリソグラフィー用リンス液組成物。

【請求項9】 請求項1記載のリンス液組成物がさらに防食剤を含有することを特徴とするリソグラフィー用リンス液組成物。

【請求項10】 防食剤がカテコール、2-ブチノール、4-ジオール、ベンゾトリアゾール及びD-ソルビトールから選ばれる少なくとも1種であることを特徴とす

る請求項9記載のリソグラフィー用リンス液組成物。

【請求項11】 請求項9記載のリンス液組成物が水溶性有機溶媒55~85重量%、水10~40重量%及び防食剤0.5~1.5重量%を含有することを特徴とするリソグラフィー用リンス液組成物。

【請求項12】 基板上に所望のレジストパターンを設けエッチング処理したのち、次の各工程で処理することを特徴とする基板の処理方法。

(I) レジストパターンをフッ化水素酸と金属を含まない塩基との塩を主要成分とする剥離液で処理する工程

(II) 基板を水溶性有機溶媒と水を含有するリソグラフィー用リンス液組成物でリンス処理する工程

(III) 水で洗浄処理する工程

【請求項13】 請求項12記載の処理方法における

(I) 工程の剥離液が(a) フッ化水素酸と金属を含まない塩基との塩、(b) ジメチルスルホキシド、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミド、N-メチル-2-ピロリドン、1,3-ジメチル-2-イミダゾリジノン、エチレングリコール及びジエチレングリコールモノブチルエーテルから選ばれる少なくとも1種、及び(c) 水を含有し、かつその水素イオン濃度(pH)が5~8の範囲にあるレジスト用剥離液であることを特徴とする基板の処理方法。

【請求項14】 (I) 工程の剥離液が(a) 成分0.2~1.0重量%、(b) 成分30~90重量%及び(c) 成分5~50重量%を含有するレジスト用剥離液であることを特徴とする請求項13記載の基板の処理方法。

【請求項15】 (I) 工程の剥離液における(a) 成分がフッ化アンモニウム、(b) 成分がジメチルスルホキシドであることを特徴とする請求項13又は14記載の基板の処理方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、リソグラフィー用リンス液組成物、さらに詳しくは、ICやLSI等の半導体素子或いは液晶パネル素子作成の際に使用する基板を剥離処理したのちリンス処理するためのリソグラフィー用リンス液組成物、及び該リソグラフィー用リンス液組成物を用いた基板の処理方法に関する。

【0002】

【従来の技術】 従来、ICやLSI等の半導体素子や液晶パネル素子は、基板上に形成されたアルミニウム、銅、アルミニウム合金等の導電性金属膜やSiO<sub>2</sub>膜等の絶縁膜上にホトレジストを均一に塗布し、それを露光又は電子線により描画したのち、現像してレジストパターンを形成し、このパターンをマスクとして前記導電性金属膜や絶縁膜を選択的にエッチングし、微細回路を形成したのち、不要のレジスト層を剥離液で除去して製造されている。

【0003】 上記レジストを除去する剥離液としては、

アルキルベシゼンスルホン酸を主要成分とした有機スルホン酸系剥離液、モノエタノールアミン等の有機アミンを主要成分とした有機アミン系剥離液、フッ化水素酸を主要成分としたフッ酸系剥離液などが挙げられる。前記有機スルホン酸系剥離液は、毒性が高いフェノール化合物やクロロベンゼン等の有機溶剤が併用されるところから作業性が悪く、また環境問題が発生する上に、基板の導電性金属膜等が腐食され易いという欠点を有する。また、有機アミン系剥離液は有機スルホン酸系剥離液に比べ毒性が低く、廃液処理に煩雑な処理が必要でなく、またドライエチング、アッシング、イオン注入などの処理で形成される変質膜の剥離性が良い上に、A1やCuなどを含む基板の腐食防止効果が優れているが、無機的性質にまで変質したレジスト膜の剥離性が充分でなく、また処理温度が60～130℃と比較的高温のため、剥離液中の可燃性有機化合物が揮発し、それに引火する危険性があるため、多額の防災施設を必要としコスト高となるなどの欠点を有する。さらにフッ化水素酸を主要成分とするフッ酸系剥離液は前記無機的変質膜の剥離性には優れているが、人体に対する安全性に問題があり取り扱い難い上に、組成物が酸性となるところから剥離槽と剥離液が入ったコンテナを結ぶ薬液供給装置等の周辺装置を腐食し易く、さらに煩雑な排気処理、廃液処理が必要であるなどの問題点がある。

## 【0004】

【発明が解決しようとする課題】上記諸問題点を解決する剥離液として、本発明者等はフッ化水素酸と金属を含まない塩基との塩を主要成分とした剥離液（以下フッ化水素酸塩系剥離液という）を既に提案している。前記フッ化水素酸塩系剥離液は低温での剥離処理が短時間で行える上に、基板上の金属薄膜や周辺装置等の腐食が防止でき、かつ毒性が低く、排気処理、廃液処理が容易に行える利点を有するが、剥離処理後の純水洗浄工程での洗浄時間が約10分間を超えると、Ti、Al、Al-Si、Al-Si-Cuなどの金属薄膜を腐食する難点がある。前記腐食はフッ化水素酸塩が水と接触することでフッ化水素酸が生じることに起因すると考え、純水をメタノール、エタノール、イソプロピルアルコール、アセトン等の有機溶媒に代えてリーン処理を行ったが、逆に基板上にフッ化水素酸塩の結晶が析出し好ましいものではなかった。

【0005】こうした現状に鑑み、本発明者等は鋭意研究を重ねた結果、フッ化水素酸塩系剥離液で剥離処理した基板をリーン処理するためのリーン液組成物を水溶性有機溶媒と水とを含有する組成物として金属薄膜の腐食が防げる上に、リーン処理後の純水洗浄液の廃液処理にかかる負担が軽減できることを見出し、本発明を完成したものである。すなわち、

【0006】本発明は、基板の金属薄膜を腐食することのないリソグラフィー用リーン液組成物を提供すること

を目的とする。

【0007】また、本発明は、該リソグラフィー用リーン液組成物を用いる基板の処理方法を提供することを目的とする。

## 【0008】

【課題を解決するための手段】上記目的を達成する本発明は、フッ化水素酸と金属を含まない塩基との塩を主要成分とする剥離液で処理した基板をリーン処理するためのリーン液組成物であって、前記リーン液組成物が水溶性有機溶媒と水とを含有する組成物であることを特徴とするリソグラフィー用リーン液組成物、及び該リソグラフィー用リーン液組成物を用いた基板の処理方法に係る。

【0009】本発明のリソグラフィー用リーン液組成物は、フッ化水素酸塩系剥離液で剥離処理した半導体素子や液晶パネル素子製造用の基板をリーン処理するためのリーン液であって、水溶性有機溶媒と水とを含有する組成物である。前記水溶性有機溶媒としては、メチルアルコール、エチルアルコール、イソプロピルアルコール等の一価のアルコール類、ジメチルスルホキシド等のスルホキシド類、ジメチルスルホン、ジエチルスルホン、ビス（2-ヒドロキシエチル）スルホン、テトラメチレンスルホン等のスルホン類、N,N-ジメチルホルムアミド、N-メチルホルムアミド、N,N-ジメチルアセトアミド、N-メチルアセトアミド、N,N-ジエチルアセトアミド等のアミド類、N-メチル-2-ピロリドン、N-エチル-2-ピロリドン、N-プロピル-2-ピロリドン、N-ヒドロキシメチル-2-ピロリドン、N-ヒドロキシエチル-2-ピロリドン等のラクタム

類、1,3-ジメチル-2-イミダゾリジノン、1,3-ジエチル-2-イミダゾリジノン、1,3-ジイソプロピル-2-イミダゾリジノン等のイミダゾリジノン類、 $\gamma$ -アブチロラクトン、 $\delta$ -バレロラクトン等のラクトン類、エチレングリコール、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノブチルエーテル、エチレングリコールモノメチルエーテルアセテート、エチレングリコールモノエチルエーテルアセテート、ジエチレングリコール、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールモノブチルエーテル等の多価アルコール類及びその誘導体が挙げられる。これらの中で、メチルアルコール、エチルアルコール、イソプロピルアルコール、ジメチルスルホキシド、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミド、N-メチル-2-ピロリドン、1,3-ジメチル-2-イミダゾリジノン、エチレングリコール及びジエチレングリコールモノブチルエーテルが好ましいが、特にメチルアルコール、エチルアルコール、イソプロピルアルコール等の一価

のアルコールがリーン液の廃液処理時に複雑な処理が不

要で安価に処理できて好ましい。

【0010】本発明のリソグラフィー用リンス液組成物は、上記水溶性有機溶媒を20～90重量%、好ましくは40～80重量%、水10～80重量%、好ましくは20～60重量%の範囲で含有する。水溶性有機溶媒が前記範囲より多いと基板上にフッ化水素酸塩の結晶が析出し易く、また少ないと金属薄膜の腐食が起こり好ましくない。

【0011】本発明のリソグラフィー用 rins 液組成物は上記成分に加えて防食剤を含有することができる。前記防食剤としては、芳香族ヒドロキシ化合物、アセチレンアルコール、カルボキシル基含有有機化合物及びその無水物、トリアゾール化合物及び糖類が挙げられる。芳香族ヒドロキシ化合物としては、具体的にフェノール、クレゾール、キシレノール、ピロカテコール、レゾルシノール、ヒドロキノン、ピロガロール、1, 2, 4-ベンゼントリオール、サリチルアルコール、p-ヒドロキシベンジルアルコール、o-ヒドロキシベンジルアルコール、p-ヒドロキシフェネチルアルコール、p-アミノフェノール、m-アミノフェノール、ジアミノフェノール、アミノレゾルシノール、p-ヒドロキシ安息香酸、o-ヒドロキシ安息香酸、2, 4-ジヒドロキシ安息香酸、2, 5-ジヒドロキシ安息香酸、3, 4-ジヒドロキシ安息香酸、3, 5-ジヒドロキシ安息香酸等を挙げることができ、中でもピロカテコールが好適である。

【0012】アセチレンアルコールとしては、具体的に  
2-ブチン-1, 4-ジオール、3, 5-ジメチル-1  
-ヘキシン-3-オール、2-メチル-3-ブチン-2  
-オール、3-メチル-1-ペンチン-3-オール、  
3, 6-ジメチル-4-オクチン-3, 6-ジオール、  
2, 4, 7, 9-テトラメチル-5-デシン-4, 7-  
ジオール、2, 5-ジメチル-3-ヘキシン-2, 5-  
ジオール等を挙げることができる。中でも2-ブチン-  
1, 4-ジオールが好適である。

【0013】カルボキシル基含有有機化合物及びその無水物としては、蟻酸、酢酸、プロピオン酸、酪酸、イソ酪酸、シュウ酸、マロン酸、コハク酸、グルタル酸、マレイン酸、フマル酸、安息香酸、フタル酸、1, 2, 3-ベンゼントリカルボン酸、グリコール酸、乳酸、リノゴ酸、クエン酸、無水酢酸、無水フタル酸、無水マレイン酸、無水コハク酸、サリチル酸等を挙げることができる。好ましいカルボキシル基含有有機化合物としては、蟻酸、フタル酸、安息香酸、無水フタル酸、及びサリチル酸があり、特にフタル酸、無水フタル酸及びサリチル酸が好適である。

【0014】トリアゾール化合物としては、ベンゾトリアゾール、o-トリルトリアゾール、m-トリルトリアゾール、p-トリルトリアゾール、カルボキシベンゾトリアゾール、1-ヒドロキシベンゾトリアゾール、ニト

ロベンゾトリアゾール、ジヒドロキシプロピルベンゾトリアゾール等を挙げることができ、中でもベンゾトリアゾールが好適である。

【0015】糖類としては、具体的にD-ソルビトール、アラビトール、マンニトール、蔗糖、澱粉等を挙げることができ、中でもD-ソルビトールが好適である。

【0016】上記各防食剤は単独でも、又2種以上を組み合わせても使用できる。

【0017】上記防食剤を含有する本発明のリソグラフィー用リンス液組成物は、水溶性有機溶媒55～85重量%、水10～40重量%、防食剤0.5～15重量%の範囲がよい。前記範囲の防食剤を含有することで金属薄膜の腐食が一段と抑制できて好適である。

【0018】上記フッ化水素酸塩系剥離液は、(a) フッ化水素酸と金属を含まない塩基との塩基を主要成分とする剥離液であり、該(a)成分を主要な成分とする剥離液であればとくに限定されないが、前記(a)成分、

(b) 水溶性有機溶媒及び (c) 水を含有し、かつ水素イオン濃度 (pH) が 5~8 の範囲にあるほぼ中性のレ

ジスト用剥離液が好適である。前記金屬を含まない塩基としては、ヒドロキシルアミン類、第1級、第2級又は第3級の脂肪族アミン、脂環式アミン、芳香族アミン、複素環式アミンなどの有機アミン、アンモニア水又は低級アルキル第4級アンモニウム塩基のように分子中に金属を含有しない塩基をいう。前記ヒドロキシルアミン類としては、具体的にヒドロキシルアミン、N,N-ジエチルヒドロキシルアミンなどが、第1級脂肪族アミンとしては、具体的にモノエタノールアミン、エチレンジアミン、2-(2-アミノエチルアミノ)エタノールなど

が、第2級脂肪族アミンとしては、具体的にジエタノールアミン、ジプロピルアミン、2-エチルアミノエタノ

ールなどが、第3級の脂肪族アミンとしては、具体的にジメチルアミノエタノール、エチルジエタノールアミンなどが、脂環式アミンとしては、具体的にシクロヘキシリアミン、ジシクロヘキシリアミンなどが、芳香族アミンとしては、具体的にベンジルアミン、ジベンジルアミン、N-メチルベンジルアミンなどが、複素環式アミンとしては、具体的にピロール、ピロリジン、ピロリドン、ピリジン、モルホリン、ピラジン、ピペリジン、N-

-ヒドロキシエチルピペリジン、オキサゾール、チアゾールなどが挙げられる。さらに低級アルキル第4級アン

モニウム塩基としては、具体的にテトラメチルアンモニウムヒドロキシド、トリメチル（2-ヒドロキシエチル）アンモニウムヒドロキシド（コリン）などが挙げられる。中でもアンモニア水、モノエタノールアミン、テトラヒドロキサン等の弱いアルカリ性の有機溶媒がよく用いられる。

トブメタルアンモニウムヒドロキシドは入手が容易である上に安全性に優れているところから好ましい。前記金属を含まない塩基とフッ化水素酸との塩は、市販のフッ化水素 50~60% 濃度のフッ化水素酸に金属を含まない塩基を pH が 5~8 となるように添加することで製造

できる。前記塩として市販のフッ化アンモニウムが使用できることはいうまでもない。前記フッ化水素酸塩系剥離液組成物のpHを5~8のほぼ中性にするには(a)成分をほぼ中性に調製すればよいが、フッ化水素酸に添加する金属を含まない塩基の種類により中性にするための含有量が異なるところから一義的に規定することができない。例えば、アンモニア水の場合、等モル濃度のフッ化水素酸とアンモニア水を等容積混合すれば目的とするpHの(a)成分が調製できる。また、エタノールアミンの場合、1モル/1のフッ化水素酸1000mLとモノエタノールアミン1モルとを混合すれば同じように(a)成分が調製できる。(a)成分のpH値が前記範囲にあることにより変質膜の剥離性の低下がなく、基板上の金属膜や蒸液供給装置などの周辺装置の腐食を抑制でき、安全に取り扱うことができる。さらに、フッ化水素の含有量が少ないとところから前記フッ化水素の発生に起因する煩雑な排気処理、廃液処理を必要とせず好適である。

【0019】上記フッ化水素酸塩系剥離液組成物の(b)成分としては、前述のリソグラフィー用リノス液組成物の水溶性有機溶媒と同様の水溶性有機溶媒が使用できる。この水溶性有機溶媒の中でもジメチルスルホキシド、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミド、N-メチル-2-ピロリドン、1,3-ジメチル-2-イミダゾリジノン、エチレングリコール及びジエチレングリコールモノブチルエーテルがレジスト変質膜の剥離性に優れ好ましい。特に、ジメチルスルホキシドが好ましい。また、(b)成分を少なくとも10重量%のエチレングリコールを含む水溶性有機溶媒とするとホール状のレジストパターンの剥離処理時に、金属蒸着板の腐食防止効果が高く、好ましい。この際、エチレングリコールの含有量が多い程腐食防止効果が向上するのでエチレングリコール単独で(b)成分としてもよいし、またジメチルスルホキシドと等重量の混合物としてもよい。

【0020】上記フッ化水素酸塩系剥離液の成分割合は、(a)成分が0.2~10重量%、好ましくは0.5~10重量%、(b)成分が30~90重量%、好ましくは40~90重量%及び(c)成分5~50重量%、好ましくは20~40重量%の範囲がよい。前記範囲で各成分が含有されることにより変質膜の剥離性、室温での剥離性、及び基板の腐食防止効果が向上する。特に剥離される基板が腐食され易い金属蒸着の基板、例えばAl、Al-Si、Al-Si-Cuなどの基板の場合には前記範囲とすることを必須とする。(a)成分が前記範囲より少ない場合には、変質膜の剥離性が低下し、多い場合には基板が腐食し易くなる。

【0021】さらに、上記フッ化水素酸塩系剥離液は(d)防食剤を含有することができる。(d)成分としては、前述のリソグラフィー用リノス液組成物の防食剤

と同様のものが使用できる。前記(d)成分を含有することでAl、Al-Si、Al-Si-Cu等の基板の変質膜の剥離性を低下することなく防食性を一段と向上できる。

【0022】上記(d)成分を含有するフッ化水素酸塩系剥離液の成分割合は、(a)成分が0.2~10重量%、好ましくは0.5~10重量%、(b)成分が30~80重量%、好ましくは40~70重量%、(c)成分が5~50重量%、好ましくは20~40重量%、(d)成分が0.5~40重量%、好ましくは、1~30重量%の範囲が好適である。各成分が前記範囲を逸脱すると、変質膜の剥離性、防食性に劣る。

【0023】本発明の基板の処理方法は、基板上に所望のレジストパターンを設けエッチング処理したのち、

(I) レジストパターンをフッ化水素酸と金属を含まない塩基との塩を主要成分とする剥離液組成物で処理する工程、(II) 基板を水溶性有機溶媒と水を含有するリソグラフィー用リノス液組成物でリノス処理する工程、および(III) 水で洗浄処理する工程からなる。前記

20 レジストパターンを設ける工程は、通常行われているパターン形成方法でよい。例えば、半導体素子や液晶パネル素子作成の際に使用されるシリコンウェーハやガラス基板などの基板にポジ型又はネガ型のレジスト組成物を回転塗布法、ロールコーティング法、バーコーティング法などの塗布法を用いて、レジスト層を形成し、次いでマスクパターンを介して紫外線、エキシマレーザーを含む遠紫外線、電子線、X線などの放射線を照射又は描画することにより潜像を形成し、アルカリ水溶液で現像し、レジストパターンを形成する方法等がある。前記剥離処理においては、浸漬法などにより室温で、1~20分間処理すればよい。また、リノス処理においては、浸漬法などにより室温で、3~20分間処理すればよい。従来の剥離処理法ではリノス処理なしで直接洗浄処理を行っていたが、繰り返し大量の水で洗浄する工程で、洗浄槽にフッ素イオンやフッ化物が増大し、廃液処理に複雑な処理を必要としたが、本発明の基板の処理方法では洗浄処理前にリノス処理をするため洗浄槽にフッ素イオンやフッ化物が残存しないので、洗浄槽中の廃液処理にかかる負担が軽減している上に、剥離処理、リノス処理、洗浄処理を連続して効率よく行える利点がある。

【0024】

【発明の実施の態様】次に、実施例により本発明をさらに詳細に説明するが、本発明はこれらの例によってなんら限定されるものではない。

【0025】

【実施例】

実施例1~6

約1.0μmのAl-Si-Cu膜を蒸着したシリコンウェーハ上にナフトキノンジアジド化合物とノボラック樹脂からなるポジ型ホトレジストであるTHMR-iP

3300（東京応化工業社製）をスピナーラー塗布して、90℃で、90秒間のプレベークを施し、膜厚2.0μmのレジスト層を形成した。このレジスト層をNSR-2005i10D（ニコン社製）を用いてマスクバターンを介して、露光し、2.38重量%のテトラメチルアンモニウムヒドロキシド水溶液で現像し、レジストパターンを形成した。次いで、120℃で90秒間のポストベークを行った。

【0026】次に、上記レジストパターンを有する約1.0μmのAl-Si-Cu膜を蒸着したシリコンウエーハをエッティング装置TSS-6000（東京応化工業社製）を用い、塩素と三塩化硼素の混合ガスをエッチャントとして、圧力5mm Torr、ステージ温度20℃で168秒間エッティング処理し、次いで、酸素とトリフルオロメタンの混合ガスを用い、圧力20mm Torr、ステージ温度20℃で30秒間アフターコロージョ

ン処理をした。前記処理後更にアッシング装置TCA-2400（東京応化工業社製）で、酸素ガスを用いて圧力0.3mm Torr、ステージ温度60℃の条件で150秒間のアッシング処理を行った。

【0027】上記処理済シリコンウエーハを、フッ化アンモニウム塩1.0重量%、ジメチルスルホキシド69.0重量%、水30重量%の剥離液に23℃で5分間浸漬し剥離処理を行った。処理した基板を表1に示す組成のリノス液でリノス処理し、さらに純水洗浄したのちの基板の腐食状態を観察した。その結果を表1に示す。

#### 【0028】比較例1

実施例1において、リノス液の組成を水のみに代えた以外は、実施例と同様にして腐食性の評価を行った。その結果を表1に示す。

#### 【0029】

【表1】

	リノス液組成	23℃で20分水に浸漬後の腐食状態
実施例1	メタノール：水 (50:50)	○
実施例2	メタノール：水 (80:20)	○
実施例3	エタノール：水 (70:30)	○
実施例4	エタノール：水 (30:70)	○
実施例5	イソプロピルアルコール：水 (70:30)	○
実施例6	イソプロピルアルコール：水 (50:50)	○
比較例1	水	×

注) 腐食状態

○：腐食なし

×：腐食あり

#### 【0030】

【発明の効果】本発明のリソグラフィー用リノス液組成物を使用することにより腐食され易いAl、Al-Si、Al-Si-Cuなどの金属薄膜に腐食が起こらな

い。また、本発明のリソグラフィー用リノス液組成物を用いた基板の処理方法にあっては、リノス処理後の純水洗浄液にフッ素イオンが極めて少量含有するにとどまるところから純水洗浄処理後の廃水処理が不要で、剥離処理、リノス処理及び洗浄処理を連続して効率よく行うことができる。

フロントページの続き

(51) Int.CI.

H01L 21/308

識別記号 庁内整理番号

F I

H01L 21/30

技術表示箇所

569E  
572B

(72) 発明者 中山 寿昌

神奈川県川崎市中原区中丸子150番地 東  
京応化工業株式会社内